

## Synthesis and Research of Alumina Ceramics Properties

Evgeniy I. Frolov<sup>ab\*</sup>, Polina V. Notina<sup>c</sup>, Sergey V. Zvonarev<sup>b</sup>,  
 Evgeniya A. Il'ina<sup>d</sup>, Vyacheslav Yu. Churkin<sup>b</sup>

a: Samara State Technical University, 244 Molodogvardeiskaya st., Samara, 443001, Russia

b: Ural Federal University, 19 Mira st., Yekaterinburg, 620000, Russia

c: Clausthal University of Technology, 2A Adolph-Roemer-Strasse, Clausthal-Zellerfeld, 38678, Germany

d: Institute of High Temperature Electrochemistry of the Ural Branch of the Russian Academy of Sciences, 20 Akademicheskaya st., Yekaterinburg, 620990, Russia

\* Corresponding author: [frolov\\_zhenya@inbox.ru](mailto:frolov_zhenya@inbox.ru)



This article belongs to the PCEE-2020 Special Issue.

© 2021, The Authors. This article is published in open access form under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).

### Abstract

The article describes in detail alumina powder synthesis by different methods at varying parameters. The technique of obtaining ceramics and the research of the optical properties for determining the materials with the maximum luminescence efficiency is presented. The concentration of the luminescence intrinsic centers and various defects differ for ceramics synthesized by different methods. It is determined that ceramics based on the powder synthesized by a sol-gel method has the maximum thermoluminescence intensity in the F-center peak, whereas for the peak of 360 °C it is obtained with the powder prepared by precipitation of aluminum nitrate with a PEG-20000 stabilizer.

### Keywords

aluminum oxide synthesis  
 thermal decomposition  
 chemical precipitation  
 sol-gel method  
 thermoluminescence

Received: 27.10.2020

Revised: 18.12.2020

Accepted: 18.12.2020

Available online: 21.12.2020

## 1. Introduction

Material optical properties are studied to create on their basis high-performance luminophores, in particular, based on aluminum oxide, which is widely used in various fields of science and technology. Aluminum oxide is used in production of ceramics obtained from the artificially synthesized substances (pure oxides, nitrides, carbides, etc.) by forming the powder followed by sintering. One of the most important stage in preparing ceramic samples is obtaining the powders which must meet a number of requirements for morphology, agglomeration, impurity and phase composition [1]. For obtaining powders with a high purity degree such synthesis methods as a precipitation method, a method of thermal decomposition and a sol-gel method are used.

The precipitation method is based on the selective distribution of components between liquid and solid phases, accompanied by the separation of one or more components from the solution in the form of a precipitate. The principle of the precipitation method is that differences in the solubility of the compounds employed are used for effective separation. Optimum separation conditions are mainly determined by the value of the solubility product. The precipitation method [2, 3] can include additional thermal

processing. Moreover, inoculating can be used for the alumina particle agglomeration process and PEG-20000 can be employed as a stabilizer [3].

Thermal decomposition of aluminum nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) is possible in two versions: using the original salt or its saturated solution. Obtaining  $\alpha\text{-Al}_2\text{O}_3$  by the decomposition is reported in [4], according to which the phase transfer in  $\alpha$ -modification occurs at a temperature higher than 1200 °C. The problem of particle sintering during nano-structures formation by the annealing method [5] under high temperatures is actively studied.

A sol-gel process was developed specifically for obtaining oxide ceramics. The process involves the following stages: preparation of alkoxide solutions, their catalytic interaction with subsequent hydrolysis, condensation polymerization, further hydrolysis [6–9]. An oxide polymer (gel) is obtained as a product. The authors of [10] describe the process of polycondensation into a gel after the hydrolysis of the polymer chains as a result of their formation upon dissolution of aluminum isopropoxide in isopropanol with the formation of complexes. After polymer chains formation their hydrolysis is carried out which results in their polycondensation into a gel. Then the gel undergoes aging, flushing out, drying and thermal processing. In [11] a modified sol-gel method for obtaining

$\text{Al}_2\text{O}_3$  is described where urea is used as a sol stabilizer  $(\text{NH}_2)_2\text{CO}$ . The disadvantage of the method is a complexity of the hardware design, and its advantage is the high purity and homogeneity of the synthesized compounds, as well as the possibility of obtaining various nanopowders [12].

Thus, the purpose of the study is to obtain aluminum oxide by various synthesis methods, to produce ceramics on its basis and to research the optical properties of the ceramics obtained.

## 2. Experimental

In the present work the experimental samples were obtained by the three methods described above. The main stages and their characteristics for each method are presented in Table 1. Next, each of them will be considered in more detail.

### 2.1. Precipitation method

The alumina oxide was obtained by the method of aluminum nitrate precipitation by the alkali (potassium hydroxide) up to pH = 9–10. Then, the “aging” took place – the exposure of the resulting mixture to air for a certain period of time. Two durations of the sample aging were taken: 2 and 48 h. A part of the samples was prepared both with inoculating and with PEG-20000. To analyze the influence of each component added, the samples were additionally prepared either only with inoculating or only with PEG-20000. However, it should be noted that the sample prepared only with inoculating was hygroscopic and its use for luminescent properties analysis was impossible. At the next stage the obtained suspensions of the samples were first filtered on a water-jet pump, and then dried at 100 °C for 12 h. The last step was a sintering process, which was conducted in two stages. The alumina synthesized powders were annealed at 700 °C for 30 min and then at 1150 °C for 4 h. The first stage is carried out for the full decay of the coprecipitation product up to the aluminum

oxide. The second stage is necessary for the transition of the alumina into  $\alpha$ -phase.

After two-stage sintering, the powders were pressed into compacts by cold static pressing at a pressure of 0.42 GPa. The compacts were of a disk shape with a diameter of 6 mm and a thickness of 1 mm. To increase the mechanical strength of the compacts, they were additionally thermally tempered in air at a temperature of 450 °C for 30 min. For these compacts, the thermoluminescence (TL) curves were measured on an experimental setup “Gray” with linear heating within the temperature range from 25 to 450 °C at a rate of 2 °/s. In order to fill the luminescence centers, before measuring TL, the samples were exposed to pulsed electron irradiation with the following characteristics: the pulse width of  $\approx 2$  ns, the average electron energy of 130 keV, the number of pulses was 10. To compare TL curves for the samples annealed at various temperatures the compacts were subjected to the additional high temperature annealing at 1200 °C, corresponding to the transfer of  $\text{Al}_2\text{O}_3$  into  $\alpha$ -phase.

The synthesized samples of  $\text{Al}_2\text{O}_3$  were examined by X-ray diffraction method (XRD). The phase analysis was done using a Rigaku D/MAX-2200VL/PC diffractometer (Rigaku, Japan) at room temperature. A curved graphite crystal was used to monochromate  $\text{Cu K}\alpha$  radiation. The data were collected over a  $2\theta$  range of 15–75° in a continuous mode at a scan rate of 3 °/min.

### 2.2. Thermal decomposition

Direct thermal decomposition of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (“chemically pure”) was conducted in two ways. The first way was to use the initial inorganic salt, to carry out thermal decomposition to amorphous alumina the temperature was first gradually raised to 250 °C (evaporation process) and then annealing took place in air at 700 °C for 30 min. The second way involved obtaining a saturated solution of aluminum nitrate by dissolving the original salt in water at its first stage.

**Table 1** Conditions of Obtaining  $\text{Al}_2\text{O}_3$  Samples

Sample No.	Synthesis method	Synthesis conditions				Annealing stages, °C (h)		
		aging, h	additives	aggregate state of the initial mixture	thermal pre-processing, °C (h.)	1	2	3
1	Precipitation method (with the drying stage after precipitation for 12 h at 100 °C)	2	-	-	-			
2								
3		48	inoculum + PEG-20000	-	-	700 (0.5)	1150 (4)	1200 (4)
4			PEG-20000	-	-			
5	Thermal decomposition	-	-	solid salt	250 (0.5)	700 (0.5)	-	1200 (4)
6								
7	Sol-gel (with a stage of evaporation to a transparent gel)	-	-	saturated solution	200 (3)	700 (1)	800 (1)	1200 (4)

Then, similar to the previous sample, evaporation and the first stage of annealing were carried out. Before annealing at the second stage, the powders were compacted at a temperature of 1200 °C for 4 h by the method described above. TL curves were measured at a temperature of 1200 °C after annealing.

### 2.3. Sol-gel method

As the initial compounds for the alumina synthesis,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$  ("reagent grade"), previously dissolved in a small amount of distilled water, were used. The obtained solutions were mixed and evaporated to a transparent gel. The gel was dried at ~200 °C for 3 h. The product obtained was annealed in air at temperatures of 700 °C (1 h), 800 °C (1 h) and 1200 °C (4 h) to remove any organic residues and soot, as well as to form the main phase of aluminum oxide. After each annealing stage the powder was ground in an agate mortar to homogenize the powder. At the final stage, similar to the previous methods, the compacts were obtained, and TL curves were measured.

## 3. Results and Discussion

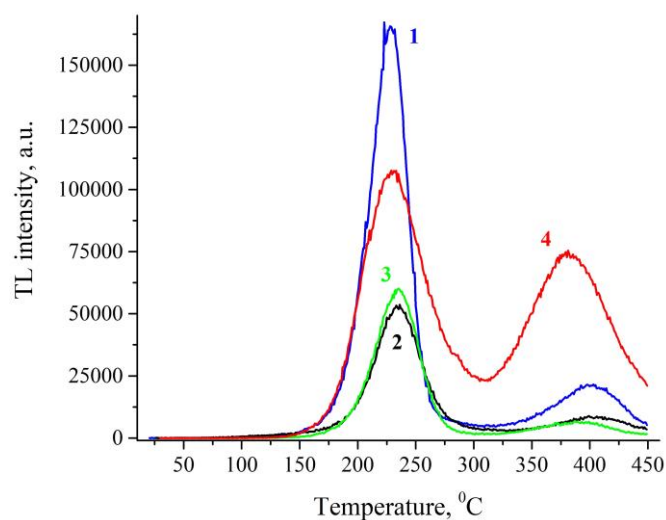
The luminescent properties of the materials under study are determined by the presence and concentration of the luminescent centers and defects, which are responsible for the luminescence at various peaks of TL curves. Fig. 1 shows ceramic TL curves annealed in air at 1150 °C produced from the alumina powder synthesized by the precipitation method at various synthesis parameters.

It is observed that two distinct peaks with maxima in the ranges 225–230 °C and 360–400 °C are recorded. The first TL peak is mostly likely to correspond to the main dosimetric peak for which various F-type alumina centers are responsible [13]. The second peak is usually associated with chromium ions which, as a rule, is found in super low concentrations in the studied oxide and has a high luminescence [14]. It should be noted that for single-crystal alumina these peaks are observed with maxima at 170 and 300 °C [15] and for the ceramics synthesized from nanopowder obtained by the sol-gel method at 140 and 330 °C [16]. The sample under study obtained by aluminum nitrate precipitation at a low aging duration without any additives has the maximum TL peak intensity at 225 °C. Moreover, the comparison of the samples with equal aging time shows that PEG-20000 additive allows the creation of ceramics with a large number of intrinsic defects, such as F-centers. In addition, such synthesis method results in creation of ceramics with the maximum luminescence intensity at the TL peak at 400 °C.

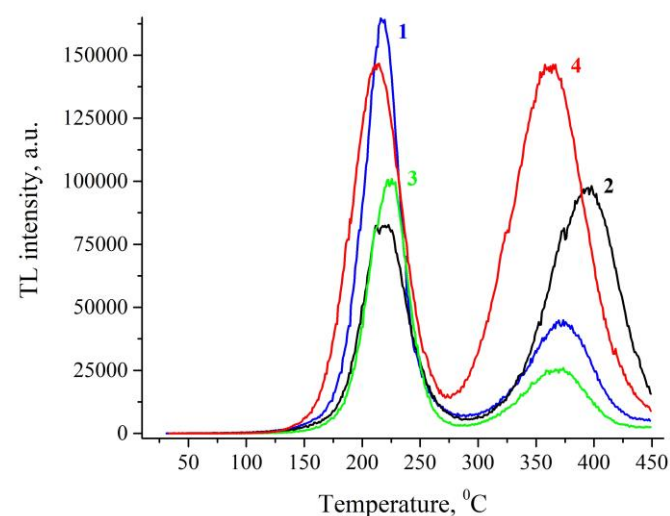
Annealing at a temperature of 1200 °C leads to a single-phase material containing only alumina  $\alpha$ -phase. Fig. 2 demonstrates ceramic TL curves shown in the previous figure (samples No. 1–4) which were additionally annealed for 4 h at a temperature of 1200 °C.

It is seen that for sample No. 1 only high temperature peak intensity changes. For the samples with the longer aging duration the intensity of the both peaks increases from 1.4 to 12.1 times. In this case, the position of the peaks does not change.

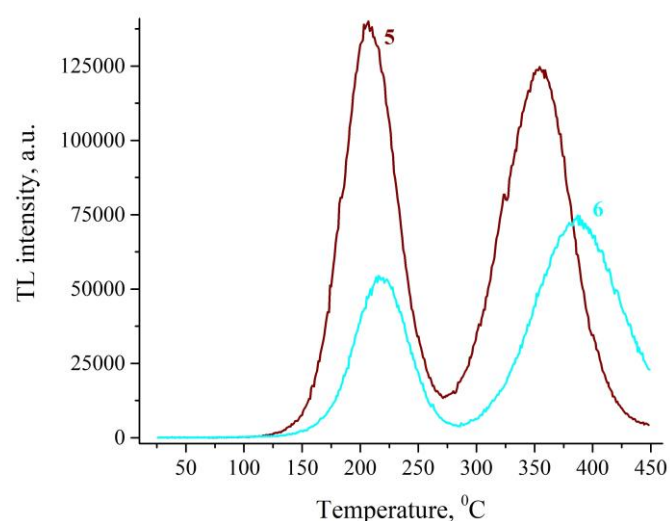
As the previous experiments showed, the transfer to alumina  $\alpha$ -phase (i.e. annealing at a temperature of 1200 °C) leads to a significant increase of luminescence in all the peaks recorded. In this regard, for the ceramics, for which the initial powder  $\text{Al}_2\text{O}_3$  was obtained by the thermal decomposition, TL curves were also measured after the last stage of annealing at 1200 °C for 4 h (Fig. 3). It is shown that the maximum concentration of F-centers occurs in a sample synthesized from a solid phase. In addition, compared to the precipitation method the position of the maximum of this peak shifts to the low-temperature region and corresponds to the range 200–215 °C. For a high-temperature peak a similar situation is observed when the peak maximum shifts to a low-temperature region and corresponds to the range 350–360 °C.



**Fig. 1** Ceramic TL curves synthesized by the precipitation method (samples No. 1–4 from Table 1) after the second annealing stage (1150 °C)



**Fig. 2** TL curves of alumina ceramics synthesized by the precipitation method at various parameters (samples No. 1–4) after additional annealing for 4 h at a temperature of 1200 °C



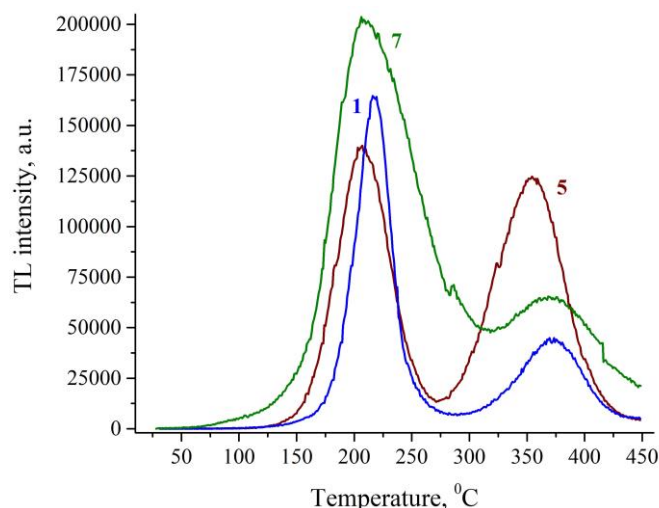
**Fig. 3** TL curves of alumina ceramics, synthesized by thermal decomposition (samples No. 5–6 from Table 1) after annealing for 4 h at 1200 °C

To compare luminescent properties of ceramics synthesized by various methods, Fig. 4 shows TL curves of the samples obtained by the methods of precipitation, thermal decomposition and sol-gel method, which have the highest luminescence intensity in F-centers luminescence band. The graph demonstrates that TL peaks of the samples mentioned differ in shape, which indicates a different nature of these centers or a possible contribution to this luminescence of additional defects of the structure obtained. Thus, the ceramics obtained by the precipitation method has the smallest peak half-width at half maximum, and the largest value is recorded for the ceramics synthesized by the sol-gel method.

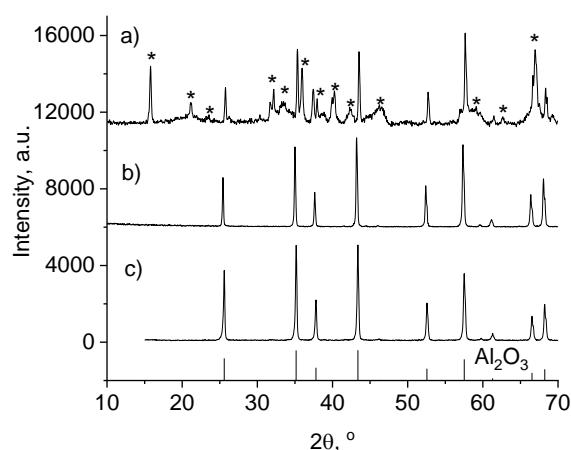
The XRF analysis was carried out to assess the influence of the structural condition on the luminescence at the recorded TL peaks. Its results are shown in Fig. 5.

## 4. Conclusions

During the study the alumina powders were obtained by various methods, such as thermal decomposition, chemical precipitation and sol-gel. The position of FWHM TL peaks with their maxima within the ranges of 200–215 °C and 350–370 °C for the ceramics obtained by various methods is different. This fact can evidence that along with the F-centers for the first peak and the luminescence centers of Chrome ions for the second peak additional defects of the obtained structure are found. Thus, in the study at the synthesis of the alumina ceramics by various methods it is determined that powder-based ceramics synthesized by the sol-gel method has the maximum TL intensity during annealing under vacuum at 1200 °C at 200 °C peak, whereas for the peak of 360 °C it occurs when the powder is prepared by the aluminum nitrate precipitation with a PEG-20000 stabilizer.



**Fig. 4** TL curves of alumina oxide synthesized by different methods: the method of precipitation (sample No. 1), thermal decomposition (sample No. 5) and a sol-gel method (sample No. 7)



**Fig. 5** Diffractogram and bar-diffractogram of  $\text{Al}_2\text{O}_3$  powders: a – precipitation method, b – thermal decomposition, c – sol-gel method; \* – phases other than  $\alpha\text{-Al}_2\text{O}_3$

## Acknowledgments

This work was financially supported by the Russian Science Foundation, project No. 18-72-10082.

## References

- Garanin SG, Rukavishnikov NN, Dmitryuk AV, Zhilin AA, Mikhailov MD. Laser ceramic. 1. Production methods. *Journal of Optical Technology*. 2010;77(9):565–76. doi:[10.1364/JOT.77.000565](https://doi.org/10.1364/JOT.77.000565)
- Li H, Lu H, Wang S, Jia J, Sun H, Hu X. Preparation of a nano-sized  $\alpha\text{-Al}_2\text{O}_3$  from a supersaturated sodium aluminate solution. *Ceramics International*. 2009;35(2):901–4. doi:[10.1016/j.ceramint.2008.01.030](https://doi.org/10.1016/j.ceramint.2008.01.030)
- Bugaeva AYU. Ceramic matrix filled composite prepared by the sol-gel method. *Glass Physics and Chemistry*. 2012;38:149–54. doi:[10.1134/S108765961106006X](https://doi.org/10.1134/S108765961106006X)
- Yakovlev IV, Volodin AM, Zaikovskii VI, Stoyanovskii VO, Lapina OB, Vedyagin AA. Stabilizing effect of the carbon shell on phase transformation of the nanocrystalline alumina particles. *Ceramics International*. 2018;44:4801–6. doi:[10.1016/j.ceramint.2017.12.066](https://doi.org/10.1016/j.ceramint.2017.12.066)
- Xu R, Xu Y. *Modern Inorganic Synthetic Chemistry: Second Edition*. Changchun (China): Elsevier; 2017. 785 p.

6. Rivera T, Azorin J., Barrera M., Soto AM. Nanostructural processing of advanced thermoluminescent materials. *Radiat E Def Sol.* 2007;162:731–6. doi:[10.1080/10420150701482675](https://doi.org/10.1080/10420150701482675)
7. Pierre A. *Introduction to Sol-Gel Processing*. New York: Kluwer Academic Publishers; 1998. 685 p.
8. Bitencourt JFS, Ventieri K, Gonçalves KA, Pires EL, Mittani JC, Tatum HA. Comparison between neodymium doped alumina samples obtained by Pechini and sol-gel methods using thermo-stimulated luminescence and SEM. *J Non-Crystal.* 2010;356:2956–59. doi:[10.1016/j.jnoncrysol.2010.03.047](https://doi.org/10.1016/j.jnoncrysol.2010.03.047)
9. Khrushcheva AA. Sol-gel synthesis of composite nanoparticles based on aluminum, cerium and zirconium oxides [dissertation]. Moscow (Russia): Baikov Institute of metallurgy and materials science of the Russian Academy of Sciences; 2016. 170 p.
10. Pietrzyk B, Miszczak S, Kaczmarek Ł, Klich M. Low friction nanocomposite aluminum oxide/MoS<sub>2</sub> coatings prepared by sol-gel method. *Ceramics International.* 2018;44:8534–9. doi:[10.1016/j.ceramint.2018.02.055](https://doi.org/10.1016/j.ceramint.2018.02.055)
11. Vinogradov VV, Agafonov AV, Vinogradov AV, Gulyaeva TI, Drozdov VA, Likholobov VA. Sol-gel synthesis, characterization and catalytic activity of mesoporous  $\gamma$ -alumina prepared from boehmite sol by different methods. *Journal of Sol-Gel Science and Technology.* 2010;56:333–9. doi:[10.1007/s10971-010-2310-x](https://doi.org/10.1007/s10971-010-2310-x)
12. Rempel' AA, Valeeva AA. *Materialy i metody nanotekhnologii* [Materials and methods of nanotechnology]. Yekaterinburg: Ural. un-ta; 2015. 136 p. Russian.
13. Grigorjeva L., Zolotarjovs A, Millers D, Smits K, Krug P, Stollenwerk J, Osman A, Tenostendarp T. Magnetron sputtering fabrication of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>:Cr powders and their thermoluminescence properties. *Radiation Measurements.* 2018;119:140–3. doi:[10.1016/j.radmeas.2018.10.009](https://doi.org/10.1016/j.radmeas.2018.10.009)
14. Kortov V., Kiryakov A., Pustovarov V. Luminescent properties of alumina ceramics doped with chromium oxide. *IOP Conf Series: J Phys: Conf Series.* 2016;741:012195. doi:[10.1088/1742-6596/741/1/012195](https://doi.org/10.1088/1742-6596/741/1/012195)
15. Kortov VS, Zvonarev SV, Pustovarov VA, Slesarev AI. Features of thermoluminescence in anion-defective alumina single crystals after highdose irradiation. *Radiation Measurements.* 2014;61:74–7. doi:[10.1016/j.radmeas.2013.12.010](https://doi.org/10.1016/j.radmeas.2013.12.010)
16. Zvonarev SV, Kortov VS, Shtang TV, Ananchenko DV, Petrovykh KA. Effect of structural changes on luminescent and dosimetric properties of nanoscale aluminum oxide. *Applied Radiation and Isotopes.* 2015;95:44–7. doi:[10.1016/j.apradiso.2014.10.003](https://doi.org/10.1016/j.apradiso.2014.10.003)